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LETTERS

Cu(I) Catalyzed or Promoted Metallacycle Transfer of Zirconacycles to Stannacycles

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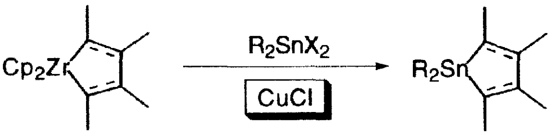
Abstract: Zirconacyclopentadienes, zirconacyclopentenes and zirconacyclopentanes were readily transferred to the corresponding stannacycles in the presence of a catalytic or a stoichiometric amount of CuCl. Without CuCl, the above transfer did not proceed at all or proceeded very slowly. A convenient one-pot procedure for the preparation of spiro stannacyclopentadiene compounds was also developed with CuCl.

Heterocycles, including stannoles, have been accepted as very important compounds in medicinal chemistry[1] and material science.[2] Fagan, Nugent and co-workers have reported a versatile synthesis of heterocycles of main group elements via "metallacycle transfer" of the carbon fragment from a 5-membered zirconacycle to a main group halide.[3] For example, a bicyclic zirconacyclopentadiene was converted into a bicyclic stannacyclopentadiene by the reaction with Me_2SnBr_2 for 2 days. Recently, we have developed a convenient preparative method of unsymmetrical monocyclic zirconacyclopentadienes from two different alkynes.[4] When we tried to prepare monocyclic stannacyclopentadienes from these zirconacyclopentadienes according to the reported method,[3] we found that the reactions did not proceed at all or proceeded extremely slowly. Actually, prolonged reaction time and high reaction temperature (for example, 3 days and refluxing THF) were required in the reported procedure, not only for the preparation of bicyclic stannacyclopentadienes, but also for the preparation of stannacyclopentenes and stannacyclopentanes from zirconacyclopentenes and zirconacyclopentanes, respectively.[3] The unsatisfactory results prompted us to develop a general method for the preparation of these 5-membered stannacycles. Here in this paper we would like to report CuCl promoted "metallacycle transfer" from zirconacycles to stannacycles (eq. 1).



(1)

When an equimolar amount of dimethyltin dichloride was added to monocyclic tetraethylzirconacyclopentadiene **1a** prepared *in situ* according to Negishi's method,[4] formation of **2a** was not detected at all even after 48h at an ambient temperature (eq. 2). Surprisingly, when the same reaction was carried out in the presence of 10 mol% of CuCl, **2a** was formed in 84% isolated yield after 1h. Typical

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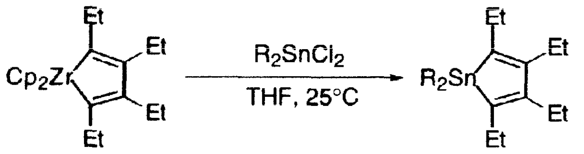
procedure is as follows. To the THF solution of zirconacyclopentadiene **1a** (3 mmol), prepared *in situ* from Cp_2ZrBu_2 (Negishi reagent, 3 mmol) and 3-hexyne (6 mmol),[4] were added Me_2SnCl_2 (3 mmol, 660 mg) and CuCl (0.3 mmol, 30 mg) at room temperature. After the reaction mixture was stirred at room temperature for 1h, the solvent was removed under reduced pressure. The residue was extracted with hexane (5 mL x 2) and filtered. Distillation under reduced pressure afforded the desired product **2a** (84% isolated yield). Diphenyltin dichloride showed a similar reactivity, and **2b** was isolated in 72% yield after 3h.



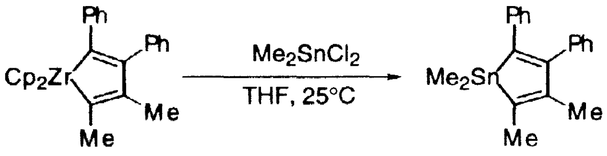
1a

2a: R = Me
2b: R = Ph

(2)

with CuCl (10 mol%), **2a**: 1h, 84%
2b: 3h, 72%
without CuCl, **2a** , **2b**: 1h, 0%; 48h, 0%

Unsymmetrically substituted zirconacyclopentadiene **1c**[5] could be also easily transferred to the corresponding stannacyclopentadiene **2c** in 83% yield in the presence of a catalytic amount of CuCl (eq. 3). The addition of a catalytic amount of CuCl facilitated the zirconacycle transfer very remarkably. Without addition of CuCl, **2c** was formed only in 40% yield even after 48h.



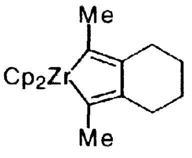
1c

2c

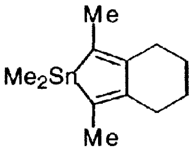
(3)

with CuCl (10 mol%), 1h, 83%
without CuCl, 1h, 22%; 48h, 40%

It was reported that the bicyclic stannacyclopentadiene **2d** was formed in 2 days without CuCl.[3] Even in the case of this bicyclic zirconacyclopentadiene **1d**, a similar effect of CuCl was observed. The reaction completed in a quantitative yield within 3h at room temperature in the presence of a catalytic amount (10 mol%) of CuCl.

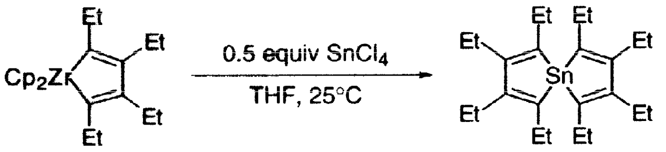


1d



2d

Based on these results, we assumed that treatment of zirconacyclopentadienes with 0.5 equiv of tetrachlorotin in the presence of CuCl would lead to the formation of spiro stannacyclopentadienes. As shown in eq. 4, the reaction of zirconacyclopentadiene **1a** with $SnCl_4$ (0.5 equiv) in the presence of a catalytic amount of CuCl (10 mol%) afforded the expected spiro stannacyclopentadiene **3**[6] in 86% isolated yield at room temperature after 3h. The compound **3** was not detected at all after 48h without addition of CuCl. This result provides a convenient one-pot procedure for the preparation of spiro stannacyclic compounds. The effect of CuCl can be explained by the transmetallation from Zr to Cu, as we already reported.[7]

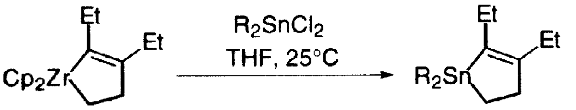


1a **3**

(4)

with CuCl (10 mol%), 3h, 86% isolated yield
without CuCl, 3h, 0%; 48h, 0%.

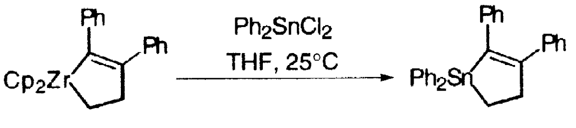
The remarkable accelerating effect of CuCl on transferring zirconacyclopentadienes into stannacyclopentadienes was also realized when zirconacyclopentenes and zirconacyclopentanes were treated with diorganotin dichlorides. Treatment of zirconacyclopentene **4a**[5] with dimethyltin dichloride or diphenyl dichloride did not give any formation of the desired products **5a** or **5b** even after 48h at room temperature (eq. 5). Again interestingly, when we carried out the same reactions with CuCl, the reactions finished within 1h at room temperature and afforded **5a** and **5b** in quantitative yields, respectively. (eq. 5). Similarly, **4c**[5] was transferred to its corresponding stannacycle **5c** in 90% yield after 1h at room temperature in the presence of CuCl. In the absence of CuCl, the stannacycle **5c** was not formed at all even after 48h (eq. 6).



4a

(5)

5a: R = Me
5b: R = Ph
with CuCl (1 equiv.), **5a**: 1h, quantitative
5b: 1h, quantitative
without CuCl, **5a**, **5b**: 1h, 0%; 48h, 0%

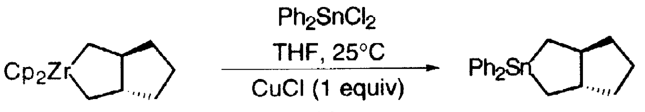


4c **5c**

(6)

with CuCl (1 equiv), 1h, 90%
without CuCl, 1h, 0%; 48h, 0%

As shown in eq. 7, transfer of zirconacyclopentane **6** into the corresponding stannacyclopentane **7** was accelerated by CuCl. Stannacyclopentane **7** was obtained in a quantitative yield at room temperature for 1h (eq. 7). In the absence of CuCl, the same compound **7** was also isolated in high yield; however, prolonged reaction time (12h) and higher reaction temperature (refluxing THF) were necessary as reported.[3]



6 **7**: 98%

(7)

We have already reported that, in the reactions of zirconacyclopentenes and zirconacyclopentanes with Me_3SnCl, a selective reaction of only one Zr-C(sp^3) bond in those zirconacycles with Me_3SnCl proceeded.[8] The other Zr-C(sp^2) or Zr-C(sp^3) bond in zirconacyclopentenes or zirconacyclopentanes was inert toward Me_3SnCl even in the presence of an excess of Me_3SnCl.[8] Similarly, in the reaction of zirconacyclopentenes and zirconacyclopentanes with Me_2SnCl_2 in the absence of CuCl, the formation of the acyclic homoallyltin or alkyltin compounds was observed. The intramolecular reaction of the Sn-Cl with the second remaining Zr-C to produce a stannacycle was very slow. The addition of CuCl in these reactions accelerated the intramolecular cyclization reaction of Sn-Cl with the second Zr-C bond.[9,10]

In this paper, we showed a consecutive transmetallation process from Zr to Cu and then Cu to Sn. Although transmetallation of Sn-C bonds to Cu-C bonds has been demonstrated,[11,12] transmetallation of Cu-C bonds to Sn-C bonds has not been reported to our knowledge.

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